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Lead isotopes tracing the origin of lead in an irrigated agricultural soil in Crete

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Abstract

Measurements of the concentrations and isotopic composition of Pb in soil fractions in an irrigated cultivated soil profile developed on Miocene sediments in Crete are used to estimate the significance of soil-derived versus man-induced sources. In soil samples, lead concentrations are 7.1 ± 1 µg/g at shallow depth (40 cm), and reach 9.1 µg/g near the surface (10 cm). $^{206}Pb/^{207}Pb$ values range from 1.20 in shallow samples to 1.19 in the uppermost samples. In all the samples, the isotopic composition of Pb in the residual soil fraction, i.e. essentially silicate Pb, is slightly more radiogenic than in the soil mobile fraction. Pb in the EDTA-extracted fraction is anthropogenic Pb issuing most probably from Pb emitted in Greece.

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1. Introduction

Because Pb deposits have characteristic Pb isotope compositions, Pb concentration and Pb-isotope ratios in combination can be used as a fingerprint to trace Pb to its source. Lead is present in the environment as four main isotopes: the radiogenic isotopes ^{208}Pb, ^{206}Pb, and ^{207}Pb and the stable isotope ^{204}Pb. In environmental sciences, because of the frequently ICP-MS use, the $^{206}Pb/^{207}Pb$ isotope ratio is commonly adopted to trace Pb contamination in different compartments of the environment at the local to global scale. Anthropogenic Pb inputs come from different activities such as lead ore mining and smelting, coal and alkyl-lead petrol combustion… To better assess the origins of Pb in a soil irrigated with treated wastewater, sequential extraction procedures applied to the soil

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fractions were combined with lead isotopic composition determination[1]. After one seasonal period of irrigation, Pb displayed no spatial relation with the drip emitter, and the Pb-spiked treated wastewater was not identified as a Pb source[1]. Here, we focus on the spatially Pb isotopic variability around a drip emitter in the cultivated Cretan soil, to assess the Pb sources and mobility, and on the composition of accessible Pb to plants.

2. Material and methods

2.1. Study area

The experimental site was located in the Prefecture of Chania in Crete. Miocene sediments are the substratum of the local siliclastic alluvial sediments and are outcropping close to the study site. The soil is an Alfisol (Al-Fe rich soil with a clay-enriched subsoil and a relatively high fertility typical of semi-arid climates) with sand as major fraction (42-66 %) associated with clays (14-42 %) and a loamy fraction (14-26 %). Organic matter (OM) was concentrated in the uppermost 25 cm (0.6 to 1.47 %).

2.2. Sequential extractions and lead isotopic measurements

Pre-irrigation soil sampling (over the whole soil column) and post-irrigation soil sampling was realized according to a defined depth-distance pattern. Soil samples (4g) were lixiviated through a 3-step sequential extraction procedure adapted from Tessier's protocol[2]: $CaCl_2$ 10^{-2} M represents the bio-accessible fraction, EDTA,NH_4 0.05 M at pH7 is used for extracting the mobilisable fraction, and final total acid attack with HNO_3 at pH 2 is done to obtain the residual fraction[1]. A set of 12 soil samples was collected for geochemical and Pb-isotopic analyses in the vicinity of one of the 1m-spaced drip emitters at various distances (10 to 50 cm) and at three depth intervals (0-10, 10-20, 20-40 cm) after two summers of irrigation with treated wastewater. The sequential extraction procedure was conducted in clean room conditions to avoid contamination by Pb. Soil samples were analyzed for trace and major inorganic elements by ICP-MS and ICP-AES respectively. The extracted fractions were then analyzed, after purification, by Thermal Ionisation Mass Spectrometry (TIMS) for the Pb isotopes. We focused here on the $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios to be comparable with the data from the literature.

3. Results and discussion

3.1. Isotopic composition of Pb in soil fractions at the Cretan site

Lead isotopic signatures can be measured only in the exchangeable and residual fractions. Lead isotopic composition in the bio-accessible fraction ($CaCl_2/NaNO_3$ extraction) cannot be determined due to very low Pb concentrations in the leachate[1]. The EDTA extracted fraction represents metals present in the non-silicate phases, including metals complexed with organic ligands. This type of extraction is adapted to species forming oxyanions (As, Cr, Mn…) and cations (Cd, Pb, Zn...).

The bulk initial soil at depth (x=30, y=40 cm) has a Pb content of 28.84 µg/g and $^{206}Pb/^{207}Pb$ of 1.21 before any wastewater irrigation, the residual fraction being 21.6 µg/g with $^{206}Pb/^{207}Pb$ of 1.22 (Fig 1a). The bulk and residual fractions present typical signatures of agricultural Cretan soils[3] or of uncontaminated Mediterranean background soils close to Miocene sediment signatures[4]. The mobile fraction contributes as far as 21 % of the total initial bulk Pb. In strong link with the pH and pH_{PZC} of the mineral phases, the missing Pb can be adsorbed on Fe-oxides, clays and organic matter[5].

After an irrigation season, the Pb concentration of the residual fraction has decreased whereas that of the EDTA extractable fraction is constant (Fig 1a), most probably due to Pb leaching out of the system or mobility between the soil fractions. In the $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$ diagram (Fig.1a and b), the isotope signature of the residual fraction

does not evolve with depth. It is very similar to that of the natural silicate Pb originating from weathering of pre-Cambrian quartzite and gneisses[6] and can be considered as the natural Pb end-member.

The EDTA-extracted Pb fraction displays a signature slightly different from a natural labile pool[6]. $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ for both the residual and the EDTA-extracted Pb are well correlated and the calculated best fit can be interpreted as a mixing line between two end-members: (i) the residual silicate fraction of the soil, (ii) anthropogenic Pb, most probably Pb from lead emitted in Greece and Crete[7]. The proximity of local industries and of a motorway (< 500 m) explains the contribution of such an anthropic-Pb in the mobilisable Pb fraction. Results confirm that Pb from the Pb-spiked wastewater used for irrigation (Pb content of 100 µg/L, $^{206}Pb/^{207}Pb$ of 1.16) is not a contributor to the soil mobile Pb[1].

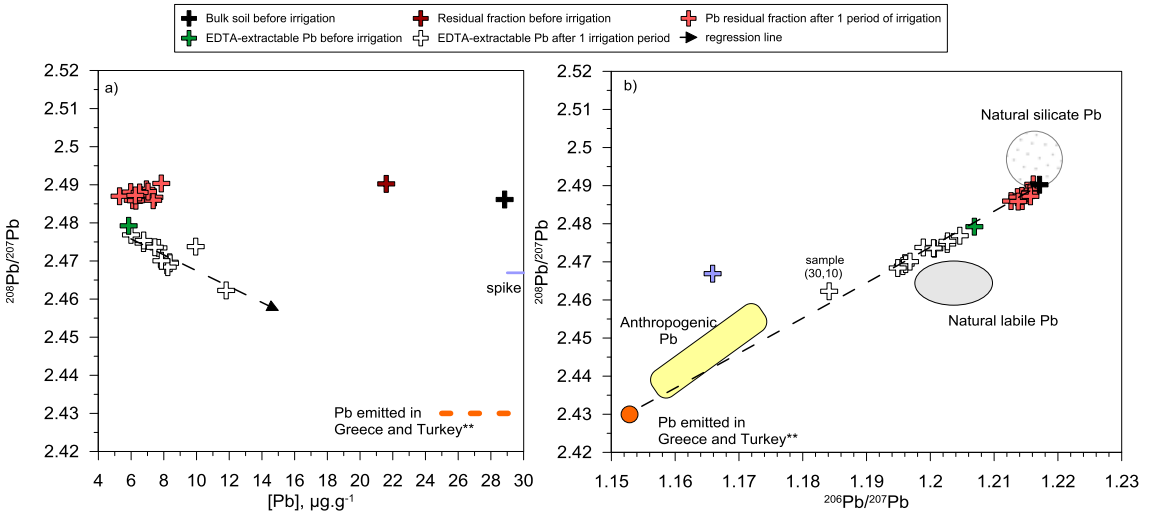

Fig. 1. Lead repartition in the studied soil at Chania. a) Lead isotope ratio $^{206}Pb/^{207}Pb$ *vs.* Pb content in the EDTA-extractable and residual fractions of the soil, and b) $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$. The reservoirs of the anthropogenic Pb, the natural labile Pb and the natural silicate Pb are from Emmanuel and Erel (2002)[7] and data** are from Erel et al. (1997)[4].

3.2. Patterns of isotopic signatures of soil Pb

Although soil labor homogenizes the top soil, the Pb content and Pb-isotopic signature was found slightly varying throughout the root zone during a year (Fig. 2). The low decrease of the EDTA-extracted Pb with depth along with a slight increase of the $^{206}Pb/^{207}Pb$ ratio from 10 to 40 cm depth is coherent with the progressive migration downwards of anthropogenic Pb after its adsorption on carrying phases such as Fe/Mn oxides and organic matter[5].

The Pb isotopic composition of the mobile fraction evolved through the irrigation season from 10 to 40 cm depth. At y=40 cm (with x=10, 20, 30, 50 cm), the mean mobile Pb is 7.1 µg/g with a mixed $^{206}Pb/^{207}Pb$ signature of 1.20 whereas at y=10 cm depth (with x=10, 20, 30, 50 cm), the mean mobile Pb is 9.1 µg/g with a mixed $^{206}Pb/^{207}Pb$ signature of 1.19. By considering that 2 µg/g were gained in the mobile fraction of the 10 cm depth sample, the mobile Pb content distribution is 78 % of mobile Pb and 22 % of new mobile Pb. A binary mixing model was then applied to calculate the Pb isotopic signature of the anthropogenic inputs in the mobile fraction. Anthropic-Pb contributing to the mobile Pb signature at the soil surface can be calculated as follows:

1.20*0.78 + Anthropic $^{206}Pb/^{207}Pb$ * 0.22 = 1.19
2.47*0.78 + Anthropic $^{208}Pb/^{207}Pb$ *0.22 = 2.47

The results give Anthropic Pb with $^{206}Pb/^{207}Pb$ = 1.16 and $^{208}Pb/^{207}Pb$ = 2.43. The results are similar when considering the mobile fraction of the initial bulk soil (6 µg/g, $^{206}Pb/^{207}Pb$ =1.21, $^{208}Pb/^{207}Pb$=2.48) with a gain of 3 µg/g of mobile Pb.

These values are more radiogenic than those measured for Israeli aerosols ($^{206}Pb/^{207}Pb$ varying from 1.12 to 1.16) and for atmospheric Pb recorded in Cairo city ($^{206}Pb/^{207}Pb$=1.15, $^{208}Pb/^{207}b$=2.43)[8] but close to lead emitted in Greece and Turkey ($^{206}Pb/^{207}Pb$ = 1.16)[7]. A mixture of lead emitted in Greece with low concentrations of Pb could account for the local Pb anthropogenic sources. This calculation thus confirms the previous mixing end-member.

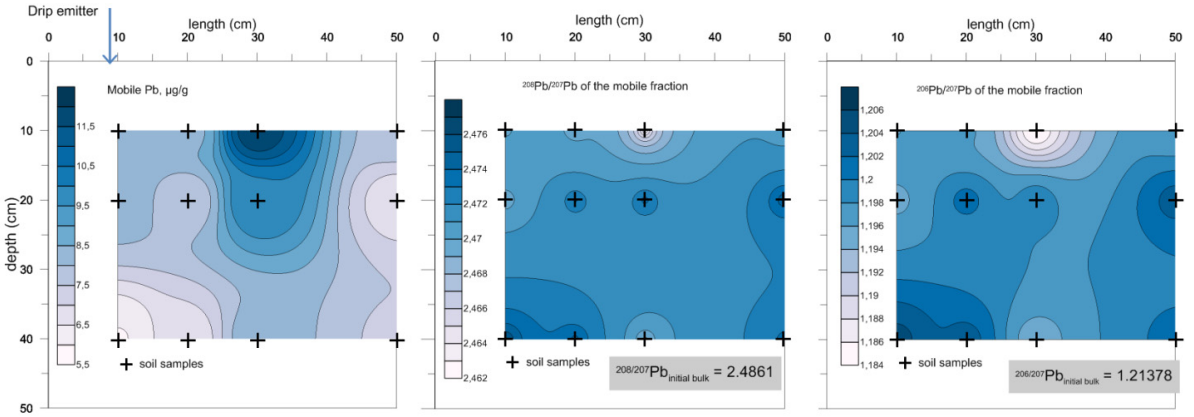

Fig. 2. Lead repartition at depth around a drip emitter in the studied soil at Chania (Crete). The Pb content, $^{208}Pb/^{207}Pb$, and $^{206}Pb/^{207}Pb$ variations are presented for the mobile EDTA-extracted fraction.

4. Conclusion

In a Cretan agricultural soil irrigated with treated wastewater, the Pb content of the soil originates from the silicate fraction and from anthropogenic-Pb produced in Greece. At all depths, there is an atmospheric contribution even if we observe a stronger natural component at 40 cm. There is an evolution towards anthropogenic Pb from pre-irrigation samples, closer to the natural background, to post-irrigation samples. This is coherent with findings on Israeli soils where petrol-derived Pb of different origins is found up to 35 cm of depth for sites close to roads. Irrigation water itself does not, in spite of the artificially increased Pb concentrations, contribute significantly to the overall soil Pb budget and to the bio-accessible and mobile soil fraction, but irrigation seems to contribute to the mobility of petrol-derived Pb by enhancing Pb transfer downwards.

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